PRODUCTION OF FUEL GRADE BIO OIL AND FUEL GAS FROM CATALYTIC PLASTIC PYROLYSIS: EFFECT OF TEMPERATURE

ELIZABETH HENDROFF

A thesis submitted in partial fulfilment of the requirements
for the award of the degree
Bachelor of Engineering (Honours) Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JANUARY 2015

ABSTRACT

As the world faces increasing depletion of petroleum resources, and environmental concern escalates, many are scurrying to find alternative energy sources that are environmentally compatible as well as able to reduce the world's dependency on petroleum resources. Plastic is a hydrocarbon that has the potential to be converted into an alternative fuel source. Thus, pyrolysis has become an increasingly explored alternative method to produce renewable energy from plastic waste. The application of specific catalyst improves the efficiency of the process and yield of the fuel gas and fuel grade bio oil produced. This research aims to synthesize and characterize Ni-Ce/Al_2O_3 as the catalyst and investigate the effect of temperature variation on the pyrolysis of Polyethylene (PE) in a catalytic reaction using a ratio of 1: 3 of catalyst: plastic to produce a high yield and quality fuel grade bio oil and fuel gas. The catalyst used in this study was synthesized to form an aqueous solution of alumina supported nickel with cerium as a promoter via the incipient wetness impregnation technique using a mass ratio of 75 wt. %, 20 wt. %, and 5 wt. % respectively and was tested in pyrolysis run at 500 ^oC to 800 ^oC. The catalyst was characterized using techniques such as Scanning Electron Microscopy (SEM), Brunauer Emmett Teller (BET) and Thermo Gravimetric Analysis (TGA). The fuel gas obtained were analysed via Gas-Chromatography-Thermal Conductivity Detector (GC-TCD) while the fuel grade bio oil produced were analysed via Gas Chromatography-Mass Spectrometry (GC-MS), Gas Chromatography-Flame Ionization Detector (GC-FID) and Fourier Transform Infrared Spectroscopy (FTIR). The findings suggest that a temperature of 700 ^oC with catalyst Ni-Ce/Al_2O_3 using a mass ratio of 20 wt. %, 5 wt. %, and 75 wt. % respectively was the most optimum temperature to run plastic pyrolysis and obtain high quality fuel gas and biofuel yield.

Keywords: pyrolysis, polyethylene, fuel gas, fuel grade bio oil, alternative energy source

ABSTRAK

Pada zaman sekarang, dunia semakin menghadapi kekurangan sumber petroleum. Ramai yang bergegas untuk mencari sumber tenaga alternatif yang tidak mengimpak alam sekitar secara negatif serta dapat mengurangkan kebergantungan dunia terhadap sumber petroleum. Plastik merupakan sejenis hidrokarbon yang berpotensi untuk dijadikan sumber bahan api alternatif. Oleh itu, pirolisis telah menjadi satu kaedah alternatif yang semakin diterokai untuk menghasilkan tenaga yang boleh diperbaharui daripada sisa plastik. Aplikasi mangkin boleh meningkatkan kecekapan proses dan hasil gas bahan api dan gred bahan api minyak yang dihasilkan. Kajian ini bertujuan untuk mensintesis dan mencirikan Ni-Ce/Al_2O_3 sebagai mangkin dan mengkaji kesan perubahan suhu pirolisis terhadap polietilena (PE) dalam tindak balas yang mengaplikasikan pemangkin dengan menggunakan nisbah 1: 3 untuk mangkin: plastik supaya memperoleh hasil dan kualiti gred bahan api minyak dan bahan api gas yang tinggi. Pemangkin yang digunakan dalam kajian ini telah disintesis untuk membentuk larutan akueus alumina disokong nikel dengan serium sebagai penganjur melalui teknik kelembapan penghamilan masing-masing menggunakan nisbah jisim 75 wt. %, 20 wt. %, dan 5 wt. % dan telah diaplikasikan untuk pirolisis dalam suhu 500 ^oC hingga 800 ^oC. Pemangkin ini telah dicirikan menggunakan teknik seperti Mikroskopi Elektron Imbasan (SEM), *Brunauer Emmett Telle*r (BET) dan Thermo gravimetrik Analisis (TGA). Gas bahan api yang diperoleh dari pirolis dianalisis mengunakan Gas Chromatography- Themal Conductivity Detector (GC-TCD) manakala bahan api minyak yang dihasilkan pula dianalisis menggunakan Gas Chromatography-Mass spectrometry (GC-MS), Gas Chromatography-Flame Ionization Detector (GC-FID) dan Fourier Transform Infrared Spectroscopy (FTIR). Hasil kajian menunjukkan bahawa suhu 700 ^oC dengan mengaplikasikan pemangkin Ni-Ce/Al_2O_3 masing-masing menggunakan nisbah jisim 20 wt. %, 5 wt. %, dan 75 wt. % merupakan suhu yang paling optimum untuk menjalankan pirolisis plastik supaya memperoleh hasil dan kualiti bahan api gas dan minyak yang tinggi.

Kata kunci: pirolisis, polyetilena, bahan api gas, bahan api minyak, sumber tenaga alternatif

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS

%	Percentage
°C	Degree Celsius
μm	Micrometer
g	Gram
m	Meter
min	Minute
mm	Millimetre
s	Second
wt. %	Weight percentage
vol. %	Volume percentage

LIST OF ABBREVIATIONS

Al_2O_3	Alumina
BET	Brunauer Emmett Teller
Ce	Cerium
EDXS	Energy Dispersive X-Ray Spectrometry
FTIR	Fourier Transform Infrared Spectroscopy
GC-FID	Gas Chromatography- Flame Ionization Detector
GC-MS	Gas Chromatography-Mass Spectrometry
GC-TCD	Gas Chromatography-Thermal Conductivity Detector
HDPE	High Density Polyethylene
Hz	Hertz
LDPE	Low Density Polyethylene
Ni	Nickel
PE	Polyethylene
PET	Polyethylene Terephthalate
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl Chloride
SEM	Scanning Electron Microscopy
TGA	Thermal Gravimetric Analysis

1 INTRODUCTION

1.1 Background

In the last 60 years or so since it was introduced, plastics have rapidly gained favour with the general public due to its high durability, low production cost and lightweight nature. However, these very properties of plastic that make it so valuable also make its disposal highly problematic. Increasing attention has been paid to plastic waste by policymakers, scientists and the media largely due to the discovery of the Great Pacific Garbage Patch by Charles Moore in the late 1990s. Rubbish, comprised mostly of plastic, was discovered floating between California and Hawaii and was estimated at about 36,000 tonnes, unequally dispersed (Sessini, 2011). The impacts of plastic waste on our health and the environment are becoming increasingly apparent due to the fact that plastics are a relatively new material [Barnes *et al*., 2009]. Most plastic are non-biodegradable. Very few plastics are designed to be biodegradable, however they can only be broken down in a controlled environment, such as in a landfill, but it is uncertain if this will occur under other conditions especially in oceans where the temperature is colder (Song *et al*., 2009; O'Brine and Thompson, 2011). Even if plastic does eventually biodegrade, it will temporarily break into smaller fragments, which then produces 'micro plastics'.

In Malaysia, polyethylene is the most common plastic waste, and can be divided into Low Density Polyethylene (LDPE) and High Density Polyethylene (HDPE) (MPMA, 2013). Among common methods used to manage plastic waste in general are landfilling, incineration, mechanical recycling, chemical recycling and cracking. Landfilling, incineration, mechanical and chemical recycling are effective ways to deal with plastic waste. However, these methods negatively impact the environment in one way or another. Aside from that, the escalating cost of these aforementioned techniques as well as increasingly stringent legislations have become contributing factors to the list of problems faced in current plastic waste management techniques. In the midst of all these repercussions, thermal cracking has emerged as an effective alternative way to manage plastic waste. The cracking process or pyrolysis as it is also known, breaks down polymeric chains into compounds of lower molecular weight in the absence of oxygen. This process produces several fractions and the proportion of each fraction and their precise composition depends heavily on the nature of the plastic waste as well as

process conditions (Panda, 2011). The hydrocarbon oil referred to also as fuel grade bio oil makes for one of the cleanest burning fuels at present (Peavy *et al*., 1985). The potential of this method to turn waste into valuable fuel products has become increasingly recognized, and with the ever increasing generation of plastic waste, increasing studies have been conducted on how best to optimise the pyrolysis process. Catalysts have been employed to enhance the rate of reaction at lower energy consumption. The type of catalyst used in a reaction will affect the manner in which the plastic decomposes. Catalysts comprise of a promoter that acts as support and influences the catalytic property. The most common catalyst support used in commercial petroleum processes is Alumina due to greater cracking and aromatization (Adrados *et al*., 2011). In this study, cerium was employed as the catalyst promoter to decrease the effect of coking.

1.2 Motivation and statement of problem

The world economic growth is largely dependent on fossil fuels as its energy source. International Energy Outlook (2010) reported that the world consumption of liquid and petroleum products was expected to grow from 86.1 million barrels per day in 2007 to 92.1 million barrels per day in 2020, 103.9 million barrels per day in 2030, and 110.6 million barrels per day by the year 2035. At this rate, the world oil reserve can only meet world demands for the next 43 years, after which there will be insufficient fossil fuels to power the world's population and their activities. As the world faces the unavoidable depletion of fossil fuels, and concern towards the environment escalates, mankind is forced to seek out alternative energy sources (Panda, 2011). It has become crucial that mankind shift their dependence to alternative energy sources that are preferably renewable, for instance solar energy, nuclear energy and wind energy just to name a few. Obtaining liquid fuel from the pyrolysis of waste plastics is a highly feasible alternative source of energy, which can reduce the dependence of mankind on fossil fuels as the liquid fuel obtained from this method exhibits similar fuel properties to that of petroleum based fossil fuels. Panda (2011) also reports that the calorific value of the fuel produced from pyrolysis of waste plastics is comparable to that of fossil fuels, which is approximately 40 MJ/kg.

Plastics are generally non-biodegradable (Song *et al*., 2009), and plastic waste management methods such as open burning, emits large amounts of harmful gases,

which have adverse effects on the environment. The environmental challenge was to reduce the negative impacts of plastic waste management on the environment. Plastics are one of the most promising materials that can be converted into fuels. Thus, the utilization of plastic waste to produce an alternative energy source was investigated as it is not only renewable (due to the continuous availability of waste plastics), but environmentally friendly and compatible with nature as well. Among the various conversion technologies, pyrolysis of plastic waste offers a practical way to produce fuel grade bio oil while simultaneously managing plastic waste in a manner that will not harm the environment (Lopez *et al*., 2012).

In this study, a catalyst was employed to study its effect on the pyrolysis of plastic waste. The commercial packed bed catalysts, which generally consisted of nickel impregnated onto alumina supports, usually experiences coking and yields consistent losses of 10-20 wt. % per day (Magrini-Bair, *et al*., 2003; Wu and Williams, 2009). As such catalyst loss is economically intolerable, there was a need to identify and/or develop a support that would reduce coking. In this study, Cerium was added as a catalyst promoter to increase available surface area of catalyst and thus reduce coking (Nishikawa *et al*., 2008). The Ni-Ce/Al_2O_3 catalyst was previously employed in the pyrolysis of Polypropylene (Wu and Williams, 2009), and hence this time, the catalyst was investigated with Polyethylene (PE). This plastic type was chosen as it is a very common plastic in Malaysian waste streams. From previous studies, the acceptable temperature to obtain liquid fuel from plastic pyrolysis is 500 °C, however different plastic types have different decomposition temperatures (Lopez *et al*., 2011b). Therefore in this study, pyrolysis was conducted at four different temperatures between 500 ^{o}C and 800 ^{o}C to investigate the effect of temperature on pyrolysis of polyethylene (PE).

1.3 Objectives

The following are the objectives of this research:

- To synthesize and characterize Ni-Ce/Al_2O_3 as the catalyst using the incipient wetness impregnation technique.
- To investigate the effect of temperature on the pyrolysis of plastic waste in a catalytic reaction to produce a high yield and quality fuel grade bio oil and gas.

1.4 Scope of this research

The following are the scope of this research:

In order to achieve the aforementioned objectives, the following scopes were identified:

i) To prepare samples of Polyethylene by grinding in a simple laboratory grinder to a size of one mm as well as to determine the temperatures of decomposition for PE plastic via Thermal Gravimetric Analysis (TGA).

ii) To synthesize Ni-Ce/Al_2O_3 catalyst and characterize the catalyst using equipments such as Scanning Electron Microscopy (SEM) for surface morphology, Brunauer Emmett Teller (BET) method for determining specific surface area and lastly Thermal Gravimetric Analysis (TGA) for measuring weight change with temperature.

iii) To study the effect of pyrolysis on the plastic in a tube furnace with Ni-Ce/Al_2O_3 as the catalyst at temperatures between 500 ^{o}C to 800 ^{o}C using a ratio of 1: 3 of catalyst: plastic.

iv) To analyse the product distribution of the fuel grade bio oil as well as fuel gas produced via plastic pyrolysis using Gas Chromatography-Mass Spectrometry (GC-MS), Fourier Transform Infrared Spectroscopy (FTIR), Gas Chromatography-Flame Ionization Detector (GC-FID) and Gas Chromatography-Thermal Conductivity Detector.

1.5 Main contribution of this work

This thesis provides an analysis of pyrolysis as an alternative method of handling waste plastics, as well as the quality of bio grade fuel and fuel gas being produced as an alternative source of energy. With this thesis, the optimum temperature at which pyrolysis may be conducted was determined for Polyethylene. The yield and quality of fuel gas and bio grade fuel produced varies with temperature. The quality of gas and liquid fuel produced at several temperatures was analysed and a comparison was made. From this study, one will be able to conclusively determine that pyrolysis of plastic waste is indeed a very beneficial way to turn waste products into an alternative energy source as well as the best temperature for pyrolysis of polyethylene in order to obtain the highest yield of high quality bio grade fuel and fuel gas. Consequently, the compared data collected can be a good reference for other researchers in future. This will save a lot of time and cost as the process of trial and error will become unnecessary.

1.6 Organisation of this thesis

This thesis is organised in 5 chapters. The current chapter, Chapter 1, is on the Introduction. The structure of the reminder of the thesis is outlined:

Chapter 2 provides literature review pertinent to this study on the pyrolysis of plastic waste together with some statistics of plastic production and generation of plastic waste as well as the different methods of managing waste plastics.

Chapter 3 covers material selection and methodology. The materials used in this study will be discussed thoroughly as well as the procedures applied. This includes techniques used for characterization, methods used for the analysis of the liquid and gas fuel obtained, and the method of pyrolysis itself.

Chapter 4 focuses on the results of this study. In this chapter, the results obtained from the analysis of the fuel gas and fuel grade bio oil as well as characterizations of plastic sample and fresh as well as spent catalyst will be analysed.

Chapter 5 provides a summary of this thesis as well as outlines the future work which will need to be carried out in due course.

2 LITERATURE REVIEW

2.1 Overview

This chapter discusses how current plastic waste management techniques are lacking and looks at pyrolysis as an effective alternative method to deal with waste plastics that is both environmentally pleasing as well as able to produce liquid fuel and fuel gas that has the potential to replace fossil fuels as an energy source.

2.2 Introduction

Increase in plastic production and uses in emerging economies are set to continue, and it is vital that waste management infrastructures develop accordingly. Generally, most plastics are thrown away after one use, but because they are durable, they persist in the environment. Plastics could take hundreds or thousands of years to degrade (Kershaw *et al*., 2011). Among the many alternative plastic waste conversion processes that have been under scrutiny, pyrolysis has received the most attention.

2.3 Plastics

2.3.1 Defining plastics

Plastics comprise of a range of synthetic or semi synthetic polymerization products which can be shaped by exposing it to heat and pressure. Polymerization is a process by which smaller single units of similar or different molecules (monomers) combine together to form longer or larger molecules by means of a chemical reaction. These longer or larger molecules, also known as macromolecules have very different properties in comparison to their starter molecules. Many hundreds or thousands of "monomers" may combine together to form the macromolecules, also known as a polymer (Professionalplastics.com, 2014). The macromolecule may also contain other substances that can enhance the performance or economics of the plastic polymer, for example, catalysts, lubricants, plasticizers, fillers, stabilizers or colouring material, each of which either discharges a useful function during moulding or imparts some useful property to the finished product.

2.3.2 Types of plastics and their recyclability

There are two types of plastics commonly found that is, thermoplastics and thermosetting plastics. Thermoplastics are plastics that can be reshaped repeatedly by simply applying some heat to soften and remould. This process can be repeated till the plastic loses its properties. Examples of such plastics are Nylon, Polyethylene, and Polypropylene etc. These plastics are usually used to make nylon ropes, water bottles and microwavable food containers respectively. Thermosetting Plastics are the opposite of thermoplastics. They cannot be softened to reshape by the application of heat once they have been formed. Any excess heat applied to the plastic will only char the material. One example of such a plastic is phenol formaldehyde, used to make Bakelite electrical switches. Table 1 shows several types of thermoplastics and their recyclability as well as their Resin Identification Code used to identify the type of plastic resin the plastic is made out of.

Table 1: Types of plastic, their Resin Identification Number and their recyclability (Panda, 2011)

Resin Identification Code	Recycling Number	Polymer Name	Abbreviation	Example of products
	1	Polyethylene terephthalate	PET or PETE	Soft drink bottles and new containers etc
	2	High-density polyethylene	HDPE	Detergent bottles, grocery bags, toys etc
	3	Polyvinyl chloride	PVC	Pipes, shower curtains automotive parts etc

	4	Low-density polyethylene	LDPE	Plastic bags, containers and tubing etc
	5	Polypropylene	PP	Microwavable food containers, and dishware etc
	6	Polystyrene	PS	Food containers, toys, and insulation boards as well as Styrofoam etc
	7	Other plastics, such as acrylic, nylon, polycarbonate, and polylactic acid etc.	OTHER or O	A mix of plastics

Table 2 classifies the different types of plastics according to the types of fuel they can produce. Thermoplastics consisting of carbon and hydrogen are the most important feedstock for fuel production either in solid or liquid form. As shown in Table 2, PP, PE and PS thermoplastics are preferable as feedstock in the production of liquid hydrocarbons.

Table 2: Types of polymers and their products (Panda, 2011)

Type of polymer	Example of polymers	Description
Polymers comprising carbon and hydrogen	Polyethylene, Polypropylene, polystyrene.	Used as feedstock for fuel production due to its high heat value and clean exhaust gas. Thermoplastics melt to form solid fuel mixed with other combustible wastes and decompose to produce liquid fuel.

Polymers comprising Oxygen	PET, phenolic resin, polyvinyl alcohol, polyoxymethylene.	Lower heat value compared to the above plastics.
Polymers comprising nitrogen or sulphur	Nitrogen: polyamide, polyurethane Sulfur: polyphenylene sulphide.	NOx or SOx heavily present in flue gas. Flue gas cleaning is necessary to avoid the emission of hazardous components to the environment.
Polymers comprising halogens .	Polyvinyl chloride, polyvinylidene chloride, bromine-containing flame retardants and fluorocarbon polymers.	Source of hazardous and highly corrosive flue gas upon thermal treatment.

2.3.3 Generation of plastic waste

In 2009, around 230 million tonnes of plastic were produced (Mudgal *et al*., 2011). This global figure has been increasing by an average rate of 9 per cent since 1950 to a peak of 245 million tonnes in 2008, after which there was a slight drop in production. Production of plastics have levelled off in recent years, however, it is not declining and may well increase in the future as applications for plastic increase and its use continues to grow in developing and emerging economies (Global Industry Analysts, 2011). Without appropriate waste management, this will lead to increased plastic waste, which will add to the 'back log' of plastic waste already in existence.

2.3.4 Sources and characteristics of plastic waste

Waste plastics may be classified into industrial and municipal plastic waste based on their origins. Both groups have varying qualities and are hence subjected to different management strategies (Buekens and Huang, 1998). Plastic wastes make up a considerable amount of municipal wastes. Large amounts of waste plastics arise as a by-product of the industrial and agricultural industries (Balakrishnan and Guria, 2007, Toward an Era of Environmental Revolution, Japan, 2004). Of the overall total waste plastics, more than 78 wt. % of this sum comprises of thermoplastics and the remaining to thermosets (Uemura *et al.*, 2003). Some examples of thermoplastics are polyethylene, polypropylene, polystyrene and polyvinyl chloride (Plastic Wastes, 1985) which can be

recycled. Conversely, thermosets include epoxy resins and polyurethanes which cannot be recycled (Uemura, 2003).

2.3.5 Municipal plastic waste

Municipal solid waste comprises largely of household waste items, for example food containers, packaging foam, disposable kitchen utensils, cutlery, electronic equipment cases, pipes, carbonated drinks bottles, thermal insulation foams, surface coatings, fertilizer bags, wire and cable etc. The percentage of plastics in municipal solid waste has increased significantly (Scott *et al.*, 1990). Waste plastics amount to around 20 % of the volume and 8 % of the weight of all municipal solid waste in USA during 2000 which increased to 11.7 % by 2006 based on Environmental Protection Agency (EPA) 2006 reports, and in Europe it is 15–25 % in the year 2004 [Narayan *et al.*, 2001]. In China in the year 2000 and Japan in 2001 plastics constitute 13 % and 7 % respectively in MSW (Waste Management in China, 2005). Similarly in India, of the total MSW, plastic waste increased from just 0.7 % in 1971 to 9 % in 2003 (Muthaa *et al.*, 2006, Gupta *et al*, 1998). In order to recycle municipal plastic wastes, plastics must first be separated out from other household wastes. Mechanical separation equipment is currently available to separate out plastics from each other (Bahr and Kozmiensky, 1997). One example is the wet separation process that separates mixed plastics based on their density. Lower density plastics such as polyethylene and polypropylene are present in much larger quantities compared to high density plastics such as polyvinyl chloride. Consequently, recycling of municipal plastic wastes should deal with plastic like polyethylene, polypropylene.

2.3.6 Industrial plastic waste

Industrial plastic wastes are waste that arises from large plastics manufacturing, processing and packaging industries. Industrial waste plastics mainly present itself in the form of pipes and fittings, tiles and sheets, switch boxes, cable sheaths, cassette boxes, fan blades, seat coverings, battery containers and front grills. Industrial plastic wastes are generally sufficiently clean, free of contamination and are available in fairly large quantities. These plastic wastes are heterogeneous or consist of mixed resins, and are therefore unsuitable to be disposed of or handled by means of landfilling. In this case thermal cracking into hydrocarbons provides a suitable means of recycling (Buekens and Huang, 1998).

2.4 Plastic waste management techniques

As the population continues to grow, the demand for plastic products has steadily increased in the last 40 years or so. As plastics are generally non-biodegradable, they cannot be easily returned to the natural carbon cycle; hence the life cycle of plastic materials ends at waste disposal facilities (Luo *et al.*, 2007). There are several methods for disposal of municipal and industrial plastic waste, for example, landfill, incineration, and chemical recovery (Miskolczi *et al.*, 2006). Finding a suitable way to treat plastic waste is important from an energetic, environmental, economic and political point of view (Delattre *et al.*, 2001). In most developed countries, domestic organic waste, including plastics packaging, is disposed of in a land fill or by means of incineration (Green, 2001). In the year 2000, 65-70 % of plastic wastes were disposed of by land filling, while 20-25 % more via incineration. Approximately only 10 % of plastic wastes were recycled (Buekens and Huang, 1998). This figure varies slightly from country to country. The Figure 1 below shows the various methods employed to manage plastic waste.

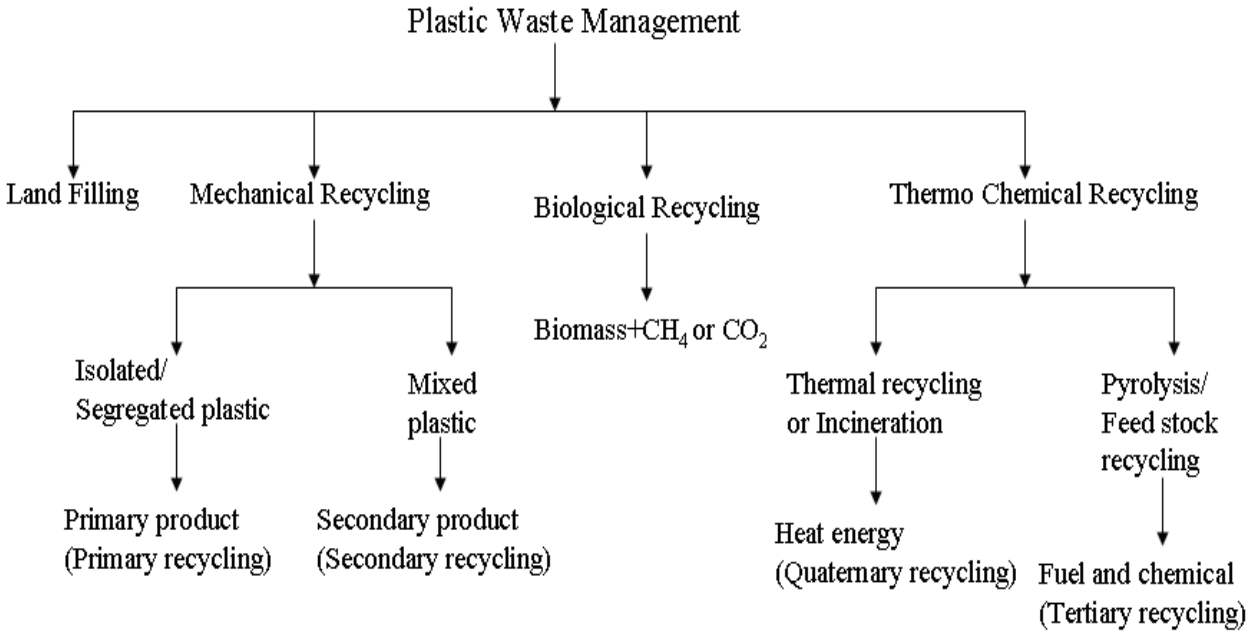

Figure 1: Plastic waste management techniques (Panda, 2011)

2.4.1 Landfilling

Most solid waste including plastics have been subjected to landfill. However, disposing of wastes via landfill has become highly undesirable due to legislative pressure (that states that landfilling must be reduced by 35 % between 1995 to 2020), rising costs, the generation of explosive greenhouse gases (for example methane) and the poor biodegradability of common plastic polymers (Garforth *et al.*, 2004). In lieu of these hazards, the Environmental Protection Agency of USA has improved federal regulations for land filling by normalizing the use of liners in the landfill bed, ground water testing for waste leaks, and post landfill closure care; however, since waste plastics have a high volume to weight ratio, appropriate landfill space is becoming both scarce and expensive. Hence other methods should be considered as an alternative way to manage waste plastics and replace land filling.

2.4.2 Mechanical Recycling

Mechanical recycling is basically reprocessing used plastics to form new similar products. Although on first sight, mechanical recycling of plastic wastes appears to be a 'green' operation, the reprocessing of waste plastics are not cost effective as high energy is required to clean, sort, transport and process as well as add additives to provide a serviceable product (Mantia, 2002). Material recycling of household waste plastics is particularly difficult as they are contaminated with biological residue or when they are a mixture of different kinds of plastics. The economic viability and practicability of such a process in an industrial application is not apparent (Plastics recycling information sheet). In this way, it is obvious that mechanical recycling, although widespread, is not a suitable method when the cost and quality of secondary produce and ecological aspects are considered.

2.4.3 Biological Recycling

Both natural and synthetic cis-poly (isoprene) becomes highly resistant to biodegradation when made into products such as tyres due to the presence of highly effective antioxidants added during their manufacture (Scott, 1997). As such, intensive research has been done to develop polymeric materials that not only fit user requirements but are also able to return to the biological cycle after their use. This has resulted in the development of biodegradable polymers which can be converted back to the biomass in a realistic time period (Scott, 1997, Scott, 1998, Scott, 2002).

Biodegradable plastics are already being used mostly in food/catering industries. They take about six weeks to photo-degrade. There is potential to use such plastics in non-packaging applications such as computer or car components. However, there are a number of concerns regarding the use of degradable plastics. Firstly, these plastics will only degrade if disposed of in appropriate conditions. For example, a photodegradable plastic product will not degrade if it is buried in a landfill site where there is no light. Secondly, they may cause an increase in methane gas emissions, which is released when materials biodegrade anaerobically. Thirdly, the use of these materials may lead to an increase in plastics waste and litter if people believe that discarded plastics will simply disappear (Plastics recycling information sheet). Due to all these problems at present the biodegraded plastics cannot substitute all the application areas of synthetic plastics.

2.4.4 Thermal recycling/Incineration

To generate energy via incineration of plastics waste is a viable method for recovered waste polymers in principle since hydrocarbon polymers replace fossil fuels as the material to be burned and thus reduce the CO_2 burden on the environment. Table 3 (Green, 2001) below shows that, the calorific value of polyethylene is similar to that of fuel oil and the thermal energy produced by incineration of polyethylene is of the same order as that used in its manufacture. Incineration is generally the preferred energy recovery option because there is financial gain by selling waste plastics as fuel (Scott, 1999). However, in most developed countries public distrust of incineration limits the potential of waste to energy technologies as it produce greenhouse gases and some highly toxic pollutants.

Table 3: Calorific values of plastics compared with conventional fuels (Green, 2001)

Fuel	**Calorific Value (MJ/kg)**
Methane	53
Gasoline	46
Fuel Oil	43
Coal	30
Polyethylene	43
Mixed Plastics	30-40

2.4.5 Pyrolysis/Feedstock recycling

Feedstock recycling, also known as chemical recycling, aims to convert waste polymers into original monomers or other valuable chemicals. These products are useful as feedstock for a variety of downstream industrial processes or as transportation fuels. There are three main approaches to feedstock recycling that is depolymerisation, partial oxidation and cracking.

2.4.6 Thermal catalytic cracking

Thermal cracking, also known as pyrolysis, is the degradation of a polymer by means of heating in the absence of oxidants. This process is usually carried out at temperatures between 350 °C and 900 °C and results in the formation of a carbon char and a volatile fraction that may be separated into condensable hydrocarbon oil consisting of paraffins, isoparaffins, olefins, naphthenes and aromatics, and a non-condensable high calorific value gas. The presence of catalyst lowers the reaction time and temperature. From an economic perspective, reducing the cost even further will make this process an even more attractive option. This method can be optimized by reuse of catalysts and the use of effective catalysts in lesser quantities. This method is promising enough to be further developed into a cost-effective commercial plastic polymer recycling process to solve severe environmental problems with plastic waste disposal.

2.4.7 Pyrolysis of plastic

As per the previous discussion, pyrolysis has been determined to be an effective method to manage plastic waste. Pyrolysis is generally defined as the controlled heating of a material in the absence of oxidants. Several studies have reported on the suitability of pyrolysis as a thermochemical recycling technique for plastics (Faravelli *et al*., 2001; Williams and Williams, 1999; Kaminsky *et al*., 1997, 2004; Kaminsky and Kim, 1999; Angyal *et al*., 2007; Demirbas, 2004; Kiran *et al*., 2000; Sakata *et al*., 2003; Lee, 2007). Pyrolysis is also known as thermal catalysis or thermolysis in brief and is a process of chemical and thermal decomposition to produce smaller molecules in the absence of oxidants (Panda, 2011). Valuable oil and gas products are formed from the pyrolysis of plastic waste. The reaction conditions used affects the product composition and properties. A lower pyrolysis temperature will produce more liquid component than gas (Williams and Williams, 1997). A higher yield was obtained from the pyrolysis of plastic waste in the presence of catalyst (Wu and Williams, 2009). The ratio of catalyst

to plastic sample in the pyrolytic reactor of 1:1 afforded the best results in the form of conversion yield in the form pyrolytic oils (Mohammad and Halim, 2009). The Ni/Al_2O_3 catalyst prepared via incipient wetness technique was shown to be a good catalyst for pyrolysis of plastics however it suffered from serious coking (Wu and Williams, 2008). In a different study, CeO_2 was added as a catalyst promoter and it was noted that coke deposition on the catalyst was reduced when the CeO_2 content was increased from 0 to 15 wt. % for the 10 wt. % $Ni/CeO_2/Al_2O_3$ catalyst. However, coke deposition was increased with further increase of CeO_2 content to 30 wt. % due to the sintering of the catalyst at 30 wt. % of CeO_2. In this thesis, the effect of temperature on the pyrolysis of plastic waste in a catalytic reaction to produce a high yield and quality fuel grade bio oil and fuel gas was investigated. $Ni\text{-}Ce/Al_2O_3$ was synthesised as the catalyst using the incipient wetness impregnation technique, using 5 wt. % Cerium only instead of CeO_2 as per previous research and was characterised by SEM, TGA and BET techniques. A ratio of catalyst to plastic sample in the pyrolytic reactor of 1:3 was used in this study, and as prior research using $Ni\text{-}CeO_2/Al_2O_3$ had only been done on Polypropylene, this research was extended to Polyethylene which is a very common plastic present in large quantities in mainstream Malaysian plastic waste. Polyethylene (PE) is among the most common non-biodegradable plastic waste available in Malaysia to date due to its widespread use in the manufacture of bottles, plastic bags, plastic film sheets etc. PE is generally divided into Low Density Polyethylene (LDPE) and High Density Polyethylene (HDPE) (MPMA, 2013). Polyethylene resin was used to simulate polyethylene waste plastics taking a ratio of 1:1 for HDPE: LDPE. This ratio was chosen because a reduction of 20 ^{o}C was reported (Lee *et al*. 2003) in the catalytic decomposition of HDPE, when LDPE was present along with HDPE. A summary of previous work was tabulated in Table 4.